

N70-78029

(ACCESSION NUMBER)

25

(THRU)

(CODE)

(PAGES)

TMX-66419

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

NO
#20
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Statistical Explanations of Thermal Diffusion in Plasmas

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The sources of electrical currents in plasmas are divided into two categories, one representing the familiar mechanical forces and the other deriving from statistical principles not found in the dynamics of individual electrons. An heuristic application to the latter of Onsager's maximization principle for the production rate of entropy yields a revised interpretation of the collisional contributions to the electron equation of motion, an explanation of thermal diffusion, and forms for the current density and heat flux that are collision-dependent through only the one parameter electrical conductivity (instead of four). Checks are provided by the rigorous kinetic theory of Chapman and Enskog.

INTRODUCTION

It has long been recognized that certain contributions (thermal diffusion, for instance) to fluxes in gases cannot be explained in terms of the ordinary mechanical forces of simple kinetic theory. Although such phenomena emerge



automatically from the rigorous kinetic theory of Chapman and Enskog,¹ the answers reveal neither the physical principles involved nor their modes of operation; consequently, some effort should be directed toward filling this gap. If the driving forces in question are not the obvious ones (electric fields and pressure gradients), they surely must be statistical in nature, whereupon the second law of thermodynamics or an extension thereof is immediately suggested.

A fundamental theorem² of irreversible thermodynamics that might apply states the following in the absence of magnetic fields:

$$\dot{S} + \dot{S}^* - \frac{1}{2} \dot{S}_c = \text{maximum}, \quad (1)$$

where \dot{S} is the total rate of entropy increase of the plasma system proper, \dot{S}^* is the rate at which entropy is yielded to the environment, and \dot{S}_c is the rate of entropy production by collisions, i.e., \dot{S}_c is the rate of dissipation of free energy. Since

$$\dot{S} = \dot{S}_c - \dot{S}^*, \quad (2)$$

Eq. (1) can be identified as the Onsager maximization principle³

$$\dot{S}_c = \text{maximum} \quad (3)$$

discussed by Kohler⁴ and by Robinson and Bernstein⁵ in their steady-state variational studies.

We, however, propose a more heuristic application of Eq. (3) than that which normally appears in work devoted to variational methods of solution of the kinetic equation. It may happen, for example, even without density

gradients, that collisions occur more frequently and thereby are capable of producing entropy more rapidly in certain regions of a plasma than in others. Since additional particles in such regions would enhance still further the overall S_e , at least the tendency of electron flows thereto must be postulated in order to satisfy Onsager's maximization principle. This, in turn, implies a statistical driving force \vec{F}_e , the exact character of which will depend on whatever criterion (most likely the collision frequency) is best suited to measure the entropy-producing efficiency of plasma regions. It is in this sense only that we explain and formulate \vec{F}_e as the driving force for thermal diffusion, such questions as concern the actual physical mechanism through which the entropy principle operates to produce \vec{F}_e being left for further consideration. Even so, much quantitative information is obtained for very little effort.

The application of Onsager's principle to a fully ionized gas with electric fields and temperature and pressure gradients (magnetic fields are more complicated and are considered only briefly) has three advantages: firstly, it suggests a revised interpretation of the momentum moment of Boltzmann's collision terms; secondly, it provides a better understanding of the origins of thermal diffusion; thirdly, it introduces forms for the current density and heat flux that are collision-dependent through only one parameter (instead of four) and which are checked by the rigorous theory. For convenience in our analysis the following model is assumed: steady-state conditions, full ionization, infinite masses for the ions which therefore serve principally as scattering centers for the electrons, zero plasma and ion flow velocities, and zero local charge

density by reason of the second-order character of Gauss' law in electrostatics. This last condition, coupled with the first, implies a system sufficiently aged for the necessary spatial distribution of ions to have occurred.

STATISTICAL FORCES

The electron equation of motion for the above conditions is found from the momentum moment of the Boltzmann equation to be

$$\frac{\partial(\rho_e \vec{v}_e)}{\partial t} = -en_e \vec{E} + \vec{j} \times \vec{B} - \nabla \cdot (\rho_e \langle \vec{c}_e \vec{c}_e \rangle) + m_e \sum_j \int \vec{c}_e (f_e' f_j' - f_e f_j) |\vec{c}_e - \vec{c}_j| b db d\alpha d\vec{c}_e d\vec{c}_j, \quad (4)$$

where n_e and ρ_e are electron number and mass densities, \vec{v}_e is the electron flow velocity, \vec{j} is the current density $= en_e \vec{v}_e$, \vec{E} and \vec{B} are electric and magnetic fields, $\langle \vec{c}_e \vec{c}_e \rangle$ is the average of the dyadic formed from the particle velocity \vec{c}_e , f_e is the electron distribution function, and b and α are the impact parameter and azimuthal angle for a binary collision. Since the standard first-order expression¹ (see Appendix A)

$$\left[\vec{c} + \frac{k}{2e} \left(\frac{m_e c_e^2}{kT_e} - 5 \right) \nabla T_e \right] \cdot \vec{c}_e - \frac{kT_e}{m_e} (\vec{c}_e \times \vec{B}) \cdot \frac{\partial \varphi_e}{\partial \vec{c}_e} = \frac{kT_e}{e} \sum_j \int f_j^{(0)} (\varphi_e' + \varphi_j' - \varphi_e - \varphi_j) |\vec{c}_e - \vec{c}_j| b db d\alpha d\vec{c}_j \quad (5)$$

obviously yields the perturbation function φ_e as a linear combination of terms, each of which contains the factor c_{ex} , c_{ey} , or c_{ez} , there can be no

v_e -contribution to $\langle \vec{c}_e \vec{c}_e \rangle$; consequently, we should equate $\nabla \cdot (\rho_e \langle \vec{c}_e \vec{c}_e \rangle)$ to the gradient of the electron pressure p_e . Additional notation in Eq. (5) includes the Maxwellian function $f_j^{(0)}$, the electron temperature T_e , and the force combination $\vec{c} = \vec{E} + (en_e)^{-1} \nabla p_e$.

Equation (4) then reduces in the steady state to

$$\vec{P}_e = en_e \vec{c} - \vec{j} \times \vec{B}, \quad (6)$$

the symbol \vec{P}_e replacing the integral terms in the original expression and clearly representing the momentum gained by electrons per unit volume per unit time due to collisions. Collisions, however, are rather tricky in that they have two entirely separate effects, each of which is pertinent to the momentum equation and particularly to \vec{P}_e : firstly, there is the obvious dynamic property whereby drag⁶ or friction forces \vec{D}_e occur between electrons and ions in relative flow motions; secondly, entropy is produced and supplied to the incompletely chaotic environment. Accordingly, we introduce the statistical force \vec{F}_s mentioned previously and write $\vec{P}_e = \vec{D}_e + \vec{F}_s$ and

$$\vec{D}_e = en_e \vec{c} - \vec{j} \times \vec{B} - \vec{F}_s. \quad (7)$$

Before proceeding with the heuristic formulation of \vec{F}_s , we find it instructive to examine a more immediate aspect of the combination of Eq. (7) with the familiar current density ($B = 0$)⁷

$$\vec{j} = \sigma \vec{c} + \alpha \nabla T_e, \quad (8)$$

the coefficients of which are the electrical conductivity σ and the thermal diffusion α . Since \vec{D}_e vanishes with \vec{e} irrespectively of ∇T_e when B is zero and \vec{F}_s is ignored (assuming this to be consistent), it is clearly possible to have currents without drags or, by similar arguments, drags without currents if thermal diffusion exists. Such predictions are surely nonsense if our concept of drag has any meaning at all; consequently, we assert that \vec{F}_s cannot be ignored in the presence of thermal diffusion, but rather is the driving force behind it. In addition, we insist upon the usual friction model

$$\sigma \vec{D}_e = en_e \vec{j}, \quad (9)$$

so that Eqs. (7) and (8) yield

$$\vec{j} = \sigma [\vec{e} - (en_e)^{-1} \vec{F}_s] \quad (10)$$

and

$$\vec{F}_s = - en_e \alpha \sigma^{-1} \nabla T_e \quad (11)$$

for $B = 0$.

Actually, this dependence of \vec{F}_s (or rather \vec{P}_e) on ∇T_e has been known for some time, but the reasons given seem incorrect. Spitzer,⁶ for example, credits the phenomenon to the velocity dependence of the collision cross sections; we shall show later, however, that rigid spheres exhibit \vec{F}_s even though the cross sections are constant. Besides, the temperature gradient per se appears to have little connection, at least directly, with

the entropy principle that was postulated in the Introduction to underlie \vec{F}_s . We therefore expect Eq. (11) to be a somewhat disguised version of what is really happening and that certain simplifications may occur if the statistical force is expressed more appropriately.

This, of course, returns us to the question of what, if not temperature, is the best criterion with which to measure the entropy-producing efficiency of plasma regions. It was suggested in the Introduction that the collision frequency provides the correct measure; accordingly, we adopt that parameter in the form of the readily available electrical resistivity η . Regions of high resistivity thus corresponding to regions of high entropy productivity, \vec{F}_s must tend⁶ to drive electrons thereto in order to enhance the production rate still further and thereby satisfy Onsager's maximization principle of Eq. (5). Hence we postulate \vec{F}_s as proportional to and in the direction of the resistivity gradient in first-order theory.

Our choice of η as the best measure of the entropy production rate clearly emphasizes electron-heavy particle collisions; in fact, no other kind contributes to the simple mean-free-path resistivity. Some credence for the desirability of this collisional property derives from the similar emphasis displayed by \vec{P}_e , the collision integral of Eq. (4) vanishing when the index j denotes electrons. Even so, electron-electron encounters do influence f_e and therefore assume a major responsibility in the effort to compensate friction (drag)-induced distortions of the Maxwellian velocity distribution. Two such current-reducing electron-electron effects are detectable: firstly, $e - e$ collisions lower σ to decrease the parts of Eq. (10) together; secondly, they modify the entropy production rates differently in different

resistivity regions so as to diminish the original cause of \vec{F}_s . Consequently, we can expect a reduction factor in \vec{F}_s of the form $\beta(Z)$, where β should decrease with decreasing ionic charge Ze because of the relative enhancement of electron-electron effects. A reasonable expression for \vec{F}_s then becomes

$$\vec{F}_s = \beta(Z)p_e v \ln \eta = -\beta(Z)p_e v \ln \sigma, \quad (12)$$

in which p_e provides the simplest means of obtaining the proper units and $\beta(Z)$, except for the general trend predicted above, is undetermined.

Equations (11) and (12) are consistent only if

$$\beta k v \sigma = e v \ln T_0, \quad (13)$$

but we shall reserve comparisons of this nature and also the determination of $\beta(Z)$ for the following section on rigorous kinetic theory. Meanwhile, the present heuristic development is completed by the substitution of Eq. (12) into Eq. (10) to give

$$\vec{j} = \sigma \left[\vec{E} + (en_e)^{-1} (v p_e + \beta p_e v \ln \sigma) \right] = \sigma \vec{E} + (en_e)^{-1} \left[v (p_e \sigma) - (1 - \beta) p_e v \sigma \right]. \quad (14)$$

An interesting property of Eq. (14), especially if $\beta = 1$, is the emphasis placed on the variation of the product $p_e \sigma$ instead of p_e alone. A certain amount of symmetry is thus introduced between the currents arising from pressure gradients and those induced by nonmagnetic statistical forces. In addition, since $(en_e)^{-1} \beta(Z) p_e v \sigma$ is identified with thermal diffusion, that phenomenon appears as the manifestation through \vec{F}_s of a statistical maximization principle (Onsager's entropy theory) and is only incidentally

involved with the temperature gradient. We shall soon discover another reason for believing Eq. (14) to be a more fundamental representation of \vec{j} than is the conventional formulation with ∇T_e .

KINETIC THEORY

The verification of Eq. (14) by kinetic theory requires the solution of the perturbation expression of Eq. (5) with $B = 0$. Since many of the details of present interest occur in Lorentz gases (large ionic charge Ze , $e-e$ collisions neglected), and since exact first-order solutions are obtained for such cases, we shall begin the analysis with this simplification and generalize later. For reasons soon to appear, all results are obtained three times - once for Coulomb potentials, again for rigid spheres of collision diameter d , and finally for the general $r^{-\delta}$ potential. A convenient notation for the simultaneous representation of these threefold answers is the bracket-semicolon-semicolon-bracket

$$\left[\text{Coulomb result; rigid sphere result; } r^{-\delta} \text{ result} \right].$$

Electron-ion collision integrals are found directly from the collision dynamics⁹ to satisfy

$$\begin{aligned} \int \left(\frac{1}{\gamma_e} - \frac{1}{\gamma_e} \right) b \, db \, d\alpha &= \frac{1}{\gamma_e} Q_{e1}^{(1)} = 2\pi \gamma_e \int (1 - \cos \chi) b \, db \\ &\approx \pi \gamma_e \left[\frac{Z^2 e^4 \ln \Lambda}{k T_e^2 \gamma_e} ; d^2 ; A(\delta) (k T_e \gamma_e^2)^{-2/\delta} \right] \\ &= \frac{8Ze^2 \gamma_e}{(2\pi m_e k T_e)^{1/2} c_L \gamma_e} \left[1 ; \frac{\gamma_e^4}{6} ; I(\delta) \gamma_e^{4(\delta-1)/\delta} \right], \end{aligned} \quad (15)$$

where $\hat{\gamma}_e$ is a unit vector in the direction of the reduced electron particle velocity $\vec{\gamma}_e = (n_e/2kT_e)^{1/2} \vec{c}_e$, $\sigma_{ei}^{(1)}$ is the electron-ion cross section, χ is the scattering angle, Λ is the ratio of the Debye length to the lower limit on b ,¹⁰ $A(\delta)$ is independent of $\vec{\gamma}_e$ and T_e , $I(\delta)$ is the integral

$$I(\delta) = \frac{1}{3} \int_0^\infty x^{(3\delta+4)/\delta} e^{-x^2} dx, \quad (16)$$

and α_L is the ordinary Lorentz electrical conductivity (\vec{E} only) given by¹¹

$$\alpha_L \approx \frac{2Ze^2}{\pi^{3/2}} \left(\frac{2kT_e}{m_e} \right)^{1/2} \left[\frac{2kT_e}{Z^2 e^4 \ln \Lambda}; \frac{1}{3d^2 kT_e}; \frac{2I(\delta)}{A(\delta)} (kT_e)^{(2-\delta)/\delta} \right]. \quad (17)$$

These expressions are exact for rigid spheres, but terms of order unity are neglected compared with $\ln \Lambda$ in the Coulomb case. It is further noted that the Coulomb and rigid sphere contributions to the bracket in the last part of Eq. (15) are special cases ($\delta = 1$ and ∞) of the $x^{-\delta}$ result. Accordingly, we write

$$\int (\hat{\gamma}_e - \hat{\gamma}_e') b db d\alpha \approx \frac{8Ze^2 I(\delta) \hat{\gamma}_e}{(2m_e kT_e)^{1/2} \alpha_L} \gamma_e^{-4/\delta}. \quad (18)$$

As can now be verified by direct substitution into the Lorentz form (see Appendix A) of Eq. (5) with $B = 0$, the perturbation function and corresponding current density and heat flux are given by

$$\psi_e = - \frac{\alpha_L \gamma_e^{4/\delta}}{4en_e I(\delta)} \left(\frac{m_e}{2kT_e} \right)^{1/2} \left[\vec{c} + \frac{k}{2e} (2\gamma_e^2 - 5) \nabla T_e \right] \cdot \hat{\gamma}_e, \quad (19)$$

$$\begin{aligned} \vec{j} &= - \frac{en_e}{\pi^{3/2}} \left(\frac{2kT_e}{m_e} \right)^{1/2} \int \gamma_e^3 \gamma_e^A \gamma_e^B e^{-\gamma_e^2} \sin \theta \, d\varphi \, d\theta \, d\gamma_e \\ &= \alpha_L \vec{E} + \frac{k\alpha_L(4-\delta)}{2e\delta} VT_e, \end{aligned} \quad (20)$$

and

$$\begin{aligned} \vec{q} &= \frac{n_e m_e}{2} \left(\frac{2kT_e}{m_e} \right)^{3/2} \int \gamma_e^5 \gamma_e^A \gamma_e^B e^{-\gamma_e^2} \sin \theta \, d\varphi \, d\theta \, d\gamma_e \\ &= - \frac{2(1+\delta)p_e}{en_e \delta} \left(\vec{j} + \frac{p_e \alpha_L}{en_e} v \ln T_e \right). \end{aligned} \quad (21)$$

The collision dependence of \vec{j} and \vec{q} is described explicitly by the two parameters δ and α_L (δ , T_e , Z , Λ or d), and we wonder if the second alone can be made to suffice.

Aside from variations in $\ln \Lambda$, which yield the second and third contributions to $2T_e \ln \Lambda \nabla \ln \alpha_L$ (Coulomb) = $(3 \ln \Lambda - 4)VT_e + (n_e k)^{-1} \nabla p_e$ and therefore must be omitted for consistency with Eqs. (15)-(21), the Lorentz conductivities of Eq. (17) are proportional to $T_e^{3/2}$, $T_e^{-1/2}$, and $T_e^{(4-\delta)/(2\delta)}$, respectively, so that

$$\nabla \alpha_L = (2T_e \delta)^{-1} \alpha_L (4 - \delta) VT_e \quad (22)$$

for all potentials ($\delta = 1$ and ∞ for Coulomb and rigid spheres). Equations (20) and (21) thus become

$$\vec{j} = \alpha_L \vec{E} + e^{-1} k T_e \nabla \alpha_L = \alpha_L \vec{E} + (en_e)^{-1} \nabla (p_e \alpha_L) \quad (23)$$

and

$$\vec{q} = - \frac{p_e}{en_e} \left(\frac{5}{2} + \frac{v \ln \alpha_L}{v \ln T_e} \right) \left(\vec{j} + \frac{p_e \sigma_L}{en_e} v \ln T_e \right), \quad (24)$$

the first of which, since $\sigma(Z = \infty) = \sigma_L$, agrees fully with Eq. (14) provided $\beta(\infty) = 1$. There is no problem with the ratio of gradients in Eq. (24) because $v\alpha_L$ and vT_e are in the same or opposite directions. Still a third representation of \vec{j} and \vec{q} is given in Appendix B.

One advantage of Eqs. (23) and (24) over the mathematically equivalent Eqs. (20) and (21) is obvious: Whereas the old set of (20) and (21) explicitly contains both δ and α_L and therefore suggests a functioning of the electron-ion force law in addition to its role in the collision frequency, the new set speaks only of the collision-frequency aspect and how it changes over a small region. Since the representation with the fewest parameters describing a particular phenomenon (collisions in this case) normally provides the most fundamental identification with physical principles, we conclude that the aforementioned multipurposiveness suggested by Eqs. (20) and (21) has no real significance.¹² This, of course, supports our earlier proposition that thermal diffusion originates more basically from $v\sigma$ than from vT_e because of the more direct association of the former with Onsager's maximization principle for entropy production rates.

It is of passing interest that the factor $(4 - \delta)$ appears both in the thermal diffusion term of Eq. (20) and in $v\alpha_L$ of Eq. (22); accordingly, the well-known failure of Maxwellian molecules ($\delta = 4$) to exhibit thermal diffusion is immediately related to the spatial constancy of the corresponding electrical

conductivity. Nonexistent in this case are the regions of higher entropy production (i.e., higher collision frequency and resistivity) toward which electrons generally must tend to flow. Additional characteristics of these very special molecules are found in the subsequent section on magnetic fields.

Now that Eq. (14) has been verified by the kinetic theory of Lorentz plasmas, it is a relatively simple matter to find $\beta(Z)$ and thereby convert to real fully ionized gases. Spitzer and Härm,¹³ for example, have computed the γ_E and γ_T reduction factors in $\sigma = \gamma_E \sigma_L$ and $\alpha = \gamma_T \alpha_L$, so that a straightforward translation (via Eqs. (12), (14), (20), and (22)) of Eq. (8) to the present analysis yields

$$\vec{j} = c\vec{E} + (en_e)^{-1} \left[v(p_e \sigma) - \gamma_E^{-1} (\gamma_E - \gamma_T) p_e v \sigma \right] \quad (25)$$

and the statistical force

$$\vec{F}_s = - \gamma_E^{-1} \gamma_T p_e v \ln \sigma. \quad (26)$$

The following properties¹³ are observed: firstly, γ_E and γ_T are functions only of Z for a given set of interaction potentials; secondly, each of γ_E and γ_T approaches unity in the Lorentz limit of infinite Z ; thirdly, $\beta(Z) = \gamma_E^{-1} \gamma_T$ decreases with decreasing Z in agreement with our speculations on the electron-electron reduction of the magnitude of \vec{F}_s .

MAGNETIC FIELDS

Statistical forces also occur when magnetic fields are applied to plasmas. For purposes of the present investigation we again assume a fully ionized

Lorentz gas, but this time with all gradients set to zero. Equation (5) for an electromagnetic field then has the solution

$$\begin{aligned} \varphi_e = & - \frac{\alpha_L \gamma_e^{4/8}}{4en_e I(\delta)} \left(\frac{m_e}{2kT_e} \right)^{1/2} \left[1 + a^2 \gamma_e^{2(4-\delta)/8} \right]^{-1} \left\{ \left[1 + a^2 \gamma_e^{2(4-\delta)/8} \right] \vec{E}_{\parallel} \right. \\ & \left. + \vec{E}_{\perp} + a \gamma_e^{(4-\delta)/8} \hat{B} \times \vec{E} \right\} \cdot \hat{\gamma}_e, \end{aligned} \quad (27)$$

where \vec{E}_{\parallel} and \vec{E}_{\perp} are the components of \vec{E} parallel and perpendicular to \hat{B} , ω is the cyclotron frequency eB/m_e , τ is the collision time $(e^2 n_e)^{-1} m_e \alpha_L$, $a = \pi^{1/2} \omega \tau [8I(\delta)]^{-1}$, and $I(\delta)$ and α_L are given by Eqs. (16) and (17).

If we now define $S_{mn}(\delta)$ as the integral

$$S_{mn}(\delta) = [3I(\delta)]^{-1} \int_0^{\infty} x^{n(m\delta+4)/\delta} \left[1 + a^2 x^{2(4-\delta)/\delta} \right]^{-1} e^{-x^2} dx, \quad (28)$$

the current density and heat flux can be written

$$\vec{j} = \alpha_L \left[\vec{E}_{\parallel} + S_{13}(\delta) \vec{E}_{\perp} + a S_{21}(\delta) \hat{B} \times \vec{E} \right] \quad (29)$$

and

$$\begin{aligned} \vec{q} = & - \frac{2(1+\delta)p_e}{en_e \delta} \left\{ \vec{j} + \frac{\alpha_L}{2(1+\delta)} \left[\delta S_{15}(\delta) - 2(1+\delta) S_{13}(\delta) \right] \vec{E}_{\perp} \right. \\ & \left. + \frac{a \alpha_L}{2(1+\delta)} \left[\delta S_{22}(\delta) - 2(1+\delta) S_{21}(\delta) \right] \hat{B} \times \vec{E} \right\}. \end{aligned} \quad (30)$$

It is observed that Eqs. (29) and (30) yield the simple mean-free-path expressions¹

$$\vec{j} = \alpha_L \left[\vec{E}_{\parallel} + (1 + \omega^2 \tau^2)^{-1} \left(\vec{E}_{\perp} + \omega \tau \hat{B} \times \vec{E} \right) \right] \quad (31)$$

and

$$\vec{q} = -5p_e (2en_e)^{-1} \vec{j} = 5n_e kT_e \vec{v}_e / 2 = \vec{h} \quad (32)$$

only for Maxwellian molecules ($\delta = 4$). The new vector \vec{h} is the enthalpy flux.

A more enlightening representation is the following set of cubic vir-expansion formulae:

$$\vec{j} \approx \alpha_L [\vec{E} - a^2 R_{31} \vec{E}_1 + a(R_{22} - a^2 R_{40}) \hat{B} \times \vec{E}] \quad (33)$$

and

$$\vec{q} - \vec{h} \approx \frac{p_e \alpha_L (\delta - 4)}{2en_e \delta} \left[\vec{E} - 3a^2 R_{31} \vec{E}_1 + 2a(R_{22} - 2a^2 R_{40}) \hat{B} \times \vec{E} \right], \quad (34)$$

where

$$R_{nm}(\delta) = [3I(\delta)]^{-1} \int_0^\infty x^{\frac{1}{\delta} + m} e^{-x^2} dx. \quad (35)$$

Equation (33) combines with Eqs. (7) and (9), and therefore with

$$\vec{j} = \alpha_L [\vec{E} - (en_e)^{-1} (\vec{F}_s + \vec{j} \times \vec{B})], \quad (36)$$

to give the magnetic statistical force

$$\vec{F}_s \approx -en_e \left[(aR_{22} - \omega\tau + a^2 \omega\tau R_{31} - a^3 R_{40}) \hat{B} \times \vec{E} - a(aR_{31} - \omega\tau R_{22}) \vec{E}_1 \right]. \quad (37)$$

Since $a(4) = \omega\tau$ and $R_{22}(4) = R_{31}(4) = R_{40}(4) = 1$, Maxwellian molecules again display a vanishing \vec{F}_s . The leading (through a^2) terms of Eq. (37) can be written

$$\begin{aligned}\vec{F}_s &\approx [a(\omega\tau)^{-1}R_{22} - 1]\vec{j} \times \vec{B} + en_e a^2 (R_{31} - R_{22}^2)\vec{E}_1 \\ &= [0.93; 0.18; 0]\vec{j} \times \vec{B} + en_e \omega^2 \tau^2 [2.15; 0.38; 0]\vec{E}_1, \quad (38)\end{aligned}$$

in which the bracket notation introduced previous to Eq. (15) is employed ($S=4$ in the third position)

As a final analysis, we compute from Eqs. (9) and (38) the total collisional momentum transfer

$$\begin{aligned}\vec{P}_e &= \vec{D}_e + \vec{F}_s = en_e (\eta_0 \vec{j}_{||} + \eta_1 \vec{j}_1 + \eta_2 \vec{j} \times \vec{B}) \\ &\approx \sigma_L^{-1} en_e \vec{j} + [a(\omega\tau)^{-1}R_{22} - 1]\vec{j} \times \vec{B} + en_e a^2 (R_{31} - R_{22}^2)\vec{E}_1, \quad (39)\end{aligned}$$

where the resistivities are defined by this expression and Eq. (33) to be

$$\eta_0 = \sigma_L^{-1}, \quad (40)$$

$$\eta_1 \approx \eta_0 [1 + a^2 (R_{31} - R_{22}^2)] = \eta_0 \{1 + \omega^2 \tau^2 [2.15; 0.38; 0]\}, \quad (41)$$

and

$$\eta_2 \approx \eta_0 (aR_{22} - \omega\tau) = \eta_0 \omega\tau [0.93; 0.18; 0]. \quad (42)$$

Spitzer,⁶ on the other hand, sets η_1 equal to η_0 (except for strong B) and never introduces the concept of a component of \vec{P}_e perpendicular to \vec{j} ; consequently, he ignores \vec{F}_s and therefore misses important contributions of order $\omega\tau$. His current density in terms of the perpendicular and Hall conductivities σ_L and σ_H , for example, becomes (to order $\omega^2 \tau^2$)

$$\vec{j} = \sigma_L \vec{E}_{||} + \sigma_L \vec{E}_1 + \sigma_H \vec{B} \times \vec{E} \approx \sigma_L \vec{E}_{||} + \sigma_L (1 - \omega^2 \tau^2) \vec{E}_1 + \sigma_L \omega\tau \vec{B} \times \vec{E}, \quad (43)$$

the comparison of which with Eq. (33) yields

$$\sigma_1(\text{present}) = \sigma_1(\text{Spitzer}) - \alpha_L(a^2 R_{31} - \omega^2 r^2) \quad (44)$$

and

$$\alpha_H(\text{present}) = \alpha_H(\text{Spitzer}) + \alpha_L^2 \eta_2. \quad (45)$$

We see from Eq. (42) that the second term on the right side of (45) is 93 percent of the first, so that Spitzer's neglect of η_2 is quite serious. The generalizations of Eqs. (44) and (45) to real plasmas are available in the work of Schweitzer and Mitchner.¹⁵

Although accurate current densities expressed in the form of the first equality of Eq. (43) are far from new,¹⁵ it is perhaps more advantageous to represent departures from simple mean-free-path theory^{6,14} by the present scheme than by the customary procedure of altering σ_1 and α_H . More specifically, we ask if η_1 different from η_0 and η_2 different from zero in Eq. (39), or equivalently \vec{F}_g different from zero in Eq. (38), can provide some clue to the underlying statistical principles. Unlike the \vec{F}_g for thermal diffusion, however, Eq. (38) has no immediate interpretation: What, for example, is the distinguishing feature of Maxwellian molecules that produces zero \vec{F}_g ? We know only of the spatially constant resistivity $\alpha_L^{-1}(\delta = 4)$ exploited earlier, but that parameter seems of little interest to the present situation. There may be some connection with the variational study by Robinson and Bernstein,⁵ particularly their discussion of two mini-max principles related in one instance to the entropy production rate and in the other to the amount of entropy stored (in the form of flows) in the system.

Even so, the translation of such concepts to simple heuristic models comparable with that of Eq. (12) is not obvious.

SUMMARY

The previously unexplained factors governing thermal diffusion in plasmas are clarified by the application of Onsager's maximization principle for the collisional production rate of entropy. This principle is the underlying cause of an electron force in the direction of and proportional to the resistivity gradient; consequently, the resulting diffusion (called thermal) is more incidentally than directly related to the temperature gradient inasmuch as the latter only provides the means by which the resistivity varies. Additional evidence that resistivity is the more basic concept derives from the fact that collision phenomena appear in less complicated forms when thermal diffusion is so expressed. Statistical forces of another character are associated with magnetic fields, but the same level of understanding is not obtained. In all cases, however, \vec{F}_S must appear in the electron equation of motion as a contributor to the momentum moment of Boltzmann's collision terms, and it is in this respect more than any other that simple mean-free-path theory fails.

Finally, as regards future research, it would be interesting to discover the actual physical mechanism through which the Onsager maximization principle operates to produce \vec{F}_S . L. D. Staton of the NASA Langley Research Center contributes the following thoughts: It seems clear that \vec{F}_S must relate to the spontaneous thermal fluctuations existing in the system. In view of the rather crude similarity between Eq. (12) and Nyquist's theorem for the thermal

noise generated by a resistor in thermal equilibrium, one suspects that it may be possible to continue in some form Rostoker's generalization¹⁶ (to thermal nonequilibrium) of the fluctuation-dissipation work of Callen and Welton,¹⁷ i.e., to remove the condition of spatial homogeneity and thereby gain a precise identification with Eq. (12). D. O. Allison, also of the Langley Research Center, is presently considering such an extension.

APPENDIX A

Equation (5) of the text derives straightforwardly from the Boltzmann equation modified by the Chapman-Enskog perturbation parameter ξ in the following way:

$$\begin{aligned} \frac{\partial f_e}{\partial t} + \vec{c}_e \cdot \nabla f_e - \frac{e}{m_e} (\vec{E} + \xi^{-1} \vec{c}_e \times \vec{B}) \cdot \frac{\partial f_e}{\partial \vec{c}_e} \\ = \xi^{-1} \sum_j \int (f_e' f_j' - f_e f_j) |\vec{c}_e - \vec{c}_j| b \, db \, d\alpha \, d\vec{c}_j, \end{aligned} \quad (A1)$$

wherein ξ^{-1} appears with the magnetic force so as to emphasize the large electron particle velocities.¹ The substitution of

$$f_e = f_e^{(0)} (1 + \xi \varphi_e) \quad (A2)$$

and

$$f_e^{(0)} = n_e \left(\frac{m_e}{2\pi kT_e} \right)^{3/2} \exp \left(- \frac{m_e c_e^2}{2kT_e} \right) \quad (A3)$$

then yields

$$\begin{aligned} \frac{\partial f_e^{(0)}}{\partial t} + \vec{c}_e \cdot \nabla f_e^{(0)} - \frac{e}{m_e} \vec{E} \cdot \frac{\partial f_e^{(0)}}{\partial \vec{c}_e} - \frac{e f_e^{(0)}}{m_e} (\vec{c}_e \times \vec{B}) \cdot \frac{\partial \varphi_e}{\partial \vec{c}_e} \\ = f_e^{(0)} \sum_j \int f_j^{(0)} (\varphi_e' + \varphi_j' - \varphi_e - \varphi_j) |\vec{c}_e - \vec{c}_j| b \, db \, d\alpha \, d\vec{c}_j \end{aligned} \quad (A4)$$

for the first-order perturbation expression.

Since $f_e^{(0)}$ depends on time only through n_e and T_e , we have $\partial f_e^{(0)} / \partial t = 0$ in the steady state considered here. Also

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$$\begin{aligned}
 \mathbf{v}_e^{(0)} &= \frac{f_e^{(0)}}{2T_e} \left(\frac{m_e c_e^2}{kT_e} - 5 \right) \mathbf{v}_e^{(0)} + \frac{f_e^{(0)}}{n_e} \mathbf{v}_{n_e} + \frac{f_e^{(0)}}{T_e} \mathbf{v}_e^{(0)} - \frac{f_e^{(0)}}{T_e} \mathbf{v}_e^{(0)} \\
 &= \frac{f_e^{(0)}}{2T_e} \left(\frac{m_e c_e^2}{kT_e} - 5 \right) \mathbf{v}_e^{(0)} + \frac{f_e^{(0)}}{p_e} \mathbf{v}_{p_e} = \frac{cf_e^{(0)}}{kT_e} \left[\vec{c} - \vec{E} + \frac{k}{2e} \left(\frac{m_e c_e^2}{kT_e} - 5 \right) \mathbf{v}_e^{(0)} \right]
 \end{aligned}
 \tag{A5}$$

and

$$\frac{\partial f_e^{(0)}}{\partial \vec{c}_e} = - \frac{m_e f_e^{(0)}}{kT_e} \vec{c}_e,
 \tag{A6}$$

so that Eq. (A4) becomes

$$\begin{aligned}
 &\left[\vec{c} + \frac{k}{2e} \left(\frac{m_e c_e^2}{kT_e} - 5 \right) \mathbf{v}_e^{(0)} \right] \cdot \vec{c}_e - \frac{kT_e}{m_e} (\vec{c}_e \times \vec{B}) \cdot \frac{\partial \varphi_e}{\partial \vec{c}_e} \\
 &= \frac{kT_e}{e} \sum_j \int f_j^{(0)} (\varphi_e' + \varphi_j' - \varphi_e - \varphi_j) |\vec{c}_e - \vec{c}_j| b \, db \, d\alpha \, d\vec{c}_j
 \end{aligned}
 \tag{A7}$$

after multiplying through by $(cf_e^{(0)})^{-1} kT_e$.

For the fully ionized Lorentz gas discussed later in the text, the right side of Eq. (A7) is written.

$$\frac{p_e c_e}{Ze} \int (\varphi_e' - \varphi_e) b \, db \, d\alpha$$

for the conditions expressed in the INTRODUCTION. This follows a little more directly from Eq. (A1) with $f_1' = f_1$, $c_1 = 0$, and especially

$$\int f_1 \, d\vec{c}_1 = n_1 = Z^{-1} n_e.$$

APPENDIX B

Equations (23) and (24) of the text may be rewritten as follows:

$$\vec{j} = \alpha_L [\vec{c} + (en_e)^{-1} p_e v \ln \alpha_L] \quad (B1)$$

and

$$\vec{q} - \vec{h} = - \alpha_L \left[\frac{p_e v \ln \alpha_L}{en_e v \ln T_e} \vec{c} + \frac{p_e^2 (9\delta^2 + 16)}{4e^2 n_e^2 \delta^2} v \ln T_e \right], \quad (B2)$$

where \vec{h} is the enthalpy flux $5n_e kT_e \vec{v}_e/2$. The standard irreversible thermodynamic formulation for generalized fluxes and forces then becomes

$$\begin{pmatrix} \vec{j} \\ \vec{q} - \vec{h} \end{pmatrix} = \alpha_L \begin{pmatrix} 1 & - \frac{p_e v \ln \alpha_L}{en_e v \ln T_e} \\ - \frac{p_e v \ln \alpha_L}{en_e v \ln T_e} & \frac{p_e^2 (9\delta^2 + 16)}{4e^2 n_e^2 \delta^2} \end{pmatrix} \begin{pmatrix} \vec{c} \\ - v \ln T_e \end{pmatrix}, \quad (B3)$$

in which Onsager's reciprocal relation is revealed by the symmetry of the coefficient matrix. No difficulty is attached to the ratio of gradients because $v \ln \alpha_L$ is always parallel or opposite to $v \ln T_e$. It is further observed that off-diagonal couplings vanish for Maxwellian molecules.

Since temperature times the local rate of irreversible entropy production (collisional) is the sum of products of corresponding generalized fluxes and forces, Eqs. (B3), (7), and (9) immediately yield

$$\begin{aligned} T_e \dot{s}_c &= \vec{c} \cdot \vec{j} - (\vec{q} - \vec{h}) \cdot v \ln T_e = (en_e)^{-1} (\vec{D}_e + \vec{F}_s) \cdot \vec{j} - (\vec{q} - \vec{h}) \cdot v \ln T_e \\ &= \alpha_L^{-1} j^2 + (en_e)^{-1} \vec{F}_s \cdot \vec{j} - (\vec{q} - \vec{h}) \cdot v \ln T_e, \end{aligned} \quad (B4)$$

the various parts of which relate the quantities normally used to describe energy dissipation.

Finally, we can use⁵

$$T_e \dot{s}_c \approx -kT_e \int \varphi_c \left(\frac{\partial f_e}{\partial t} \right)_c d\vec{c}_e \approx Z^{-1} p_e \int c_e f_e^{(0)} \varphi_e (\varphi_e - \varphi_e') p db d\alpha d\vec{c}_e \quad (B5)$$

and Eqs. (27) and (33) to compute the local energy dissipation rate for electromagnetic fields. There results the following expansion valid through a^3 :

$$\begin{aligned} T_e \dot{s}_c &\approx \alpha_L \left[E^2 - 2a^2 R_{31} E_1^2 + a^2 R_{31} (\vec{E} \times \vec{E})^2 \right] \\ &= \alpha_L (E^2 - a^2 R_{31} E_1^2) = \vec{E} \cdot \vec{J}, \end{aligned} \quad (B6)$$

a second representation of which derives from Eqs. (7), (9), (38), and (B6) to be

$$T_e \dot{s}_c = (en_e)^{-1} (\vec{D}_e + \vec{F}_e) \cdot \vec{J} \approx \alpha_L^{-1} J^2 + a^2 \alpha_L (R_{31} - R_{22}^2) E_1^2. \quad (B7)$$

ACKNOWLEDGMENT

The author is indebted to D. Adamson and L. D. Staton of the NASA, Langley Research Center, for their review and valuable comments on the original manuscript.

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